Graphene nanosheets and polyacrylic acid grafted silicon composite anode for lithium ion batteries

Birhanu Desalegn Assresahegn, Benjamin Diby Ossonon, Daniel Bélanger*

Département de Chimie, Université du Québec à Montréal, Case Postale 8888, succursale Centre-Ville, Montréal, Québec, H3C 3P8, Canada

HIGHLIGHTS

- Polyacrylic acid grafted silicon/graphene composite electrode without binder.
- Electrode with a 90 wt% silicon loading.
- Graphene additive yielded a two-fold increase in electronic conductivity.
- Stable capacity of 1200 mAh.g^{-1} for close to 600 cycles at a current of 3.4 A g^{-1}.
- Better accommodation of volume changes without the need to use a binder.

GRAPHICAL ABSTRACT
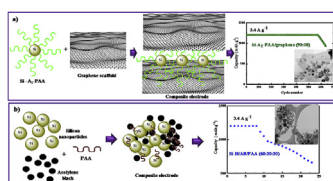
ABSTRACT

A silicon/graphene composite anode for lithium-ion batteries was fabricated with a high loading of Si by combining surface-modified silicon with graphene. The Si nanopowder was modified by a binder-like organic moeity (1-(bromoethyl) benzene and polyacrylic acid) grafted on the surface of hydrogenated silicon by diazonium chemistry and surface initiated atom transfer radical polymerization. The graphene was produced by electrochemical exfoliation of natural graphite. The optimum composite electrode prepared without a binder, with silicon loading as high as 85 wt% and a mass loading of 1.1 ± 0.1 mg cm^{-2} yielded a discharge capacity of 1020 mAh per gram of electrode mass (or 1200 mAh per gram of Si) after 586 charge/discharge cycles at a rate of 3.4 A g^{-1}. It showed first cycle Coulombic efficiency of more than 90% in the absence of electrolyte additives at a current rate of 0.05 A g^{-1}.

1. Introduction

With rising interest in the commercialization of hybrid electric vehicles (HEVs) and electric vehicles (EVs) for the automotive industry, there has been growing attention on the development of improved lithium-ion batteries (LIBs) [1]. For these technologies to be used for the desired applications, the electrode materials in LIBs must possess high energy and power densities and better cyclability than the current state of the art. Among potential anode electrode materials, silicon is an attractive candidate for high energy density next generation LIBs due to

its high theoretical capacity [2–4]. However, large scale commercialization of Si electrode is highly impeded mainly due to its continuous large volume change and pulverization upon cycling [5–7]. Consequently, this has been shown to cause continuous electrolyte degradation and solid-electrolyte interphase (SEI) growth and propagation, loss of contact within active material particles and between current collector-active materials, and increased electrical resistance which all lead to cell failure [5,7–9].

Therefore, in the past decade different strategies have been developed to improve the electrochemical performance of Si anode

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materials. The primary route is nano-structuring of Si. In principle nano-sized Si experience less structural damage and pulverization compared to bulk Si upon volume-changes because nanostructures are more effective at releasing strain [6,9]. Another approach is to add conductive carbon materials to serve as additional structural support (e.g., graphene and graphene derivatives [10–14], carbon black [15,16], graphite [17–20], carbon nanotubes [21–24] and nanofibers [25]) to form Si–carbon nanocomposites, so that the carbon material can buffer the volume change of Si and enhance the electrical conductivity of the resulting composite electrode. All of these strategies are considered to be useful for the development of Si-based anodes for practical applications. However, nano-sizing generally enhances the surface to area ratio of the active material and when used in the fabrication of electrodes, it is reported to increase the extent of undesired side reactions in the cell and result in rapid battery failure [5,26–29]. It also causes poor electrode packing density which can reduce the volumetric energy density of the overall cell. Moreover, the conducting carbon additives with relatively larger surface area were reported to be prone to adsorption of the physically mixed binder. This resulted in non-homogeneous dispersion of the binder between the active material particles or the active material particles and current collector [30]. It has also been reported that the binder molecules tend to bind together rather than adhering to the active material particles, thus contributing to the poor mechanical properties of such composite electrodes [31–36].

In view of those drawbacks, we have recently reported an approach through covalent grafting of binder-like molecules on the silicon nanoparticles surface which aids to avoid a direct contact between the active material and electrolyte by serving as artificial solid-electrolyte interphase in addition to promoting the particles self-adhesion. Those composite electrodes have shown a significant improvement in electrochemical performance particularly in terms of cyclability, decreasing the amount of binder, improve electrode mechanical and packing densities and avoiding the use of electrolyte additives [37,38]. Nevertheless, those silicon composite electrodes have shown relatively low electronic conductivity which has been attributed to the ease of oxidation of a hydrogenated silicon nano-powder under working conditions and partly due to the modifications made by the covalent grafting of the organic molecules on the active material surface [38]. For this reason the electrodes delivered modest capacity at higher charge/discharge current densities. Therefore, to improve the performance of those composite electrodes at high charge/discharge cycling rate, augmenting their electronic conductivities will have a paramount importance. Lately, compared with conventional conductive additives, graphene-based materials have led to improved electrochemical performance of silicon composite anodes at high rate due to their superior electrical conductivity [39]. Also, the exceptional mechanical properties of graphene can potentially provide skeletal support to buffer the mechanical stresses caused by volume changes in the electrode materials [2,40–45] and maintain the overall mechanical integrity of the composite electrode. Particularly, because of the 2D structure of graphene, Si-graphene composites including wrapping through sandwich structures (Fig. 1) possess a porous texture that could impart good flexibility to the composite and void space useful for electrolyte transport [46,47]. In addition, the incorporation of silicon particles in between graphene layers is also reported to inhibit the degree of restacking of graphene sheets during cycling which is anticipated to maintain the good electrical conductivity and mechanical structure of the electrode [11,47].

Silicon-graphene composite electrodes have been fabricated by various approaches such as layer by layer chemical vapor deposition [40], freeze-drying [48], sonication followed by vacuum-filtration [47,49] or mechanical blending [50]. Nonetheless, most of those methods are either not scalable or the resulting electrodes do not have acceptable electrochemical performance especially in terms of capacity and cycling life. Above all, a notable drawback of most current silicon-
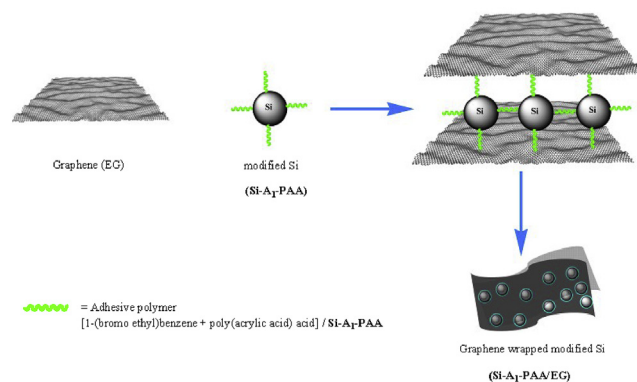

Fig. 1. Illustration of modified-silicon nanoparticles/graphene sheets structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

graphene composite electrodes is the need to use a large proportion of the graphene (most of the time more than 40%), which obviously penalizes their volumetric and gravimetric capacity (Table S1, supplementary material).

Herein, we demonstrate a method to fabricate high Si loading composite electrode by mechanical blending of modified silicon nanoparticles with graphene sheets. The graphene used in the fabrication of the electrodes was prepared by electrochemical exfoliation of natural graphite [51]. The silicon nanoparticles are synthesized by following hydrogenation, covalent grafting of a thin polymerization initiator layer by using diazonium chemistry and further addition of polyacrylic acid by atom transfer radical polymerization (ATRP) [38]. The electrochemical performance of the composite Si anodes in terms of cyclability, rate performance and required amount of electrochemically inactive components are also assessed using galvanostatic cycling.

2. Experimental part

The complete list of chemicals and reagents (with their characteristics and suppliers) used in this work can be found in the supplementary data.

2.1. Material synthesis

For the surface modification of silicon nanoparticles, the Si powder is hydrogenated (Si-H) using a 2% (v/v) solution of HF followed by grafting *1*-(bromoethyl)benzene (Si-A$_1$) using diazonium chemistry to use as initiator for the polymerization of *tert*-butyl acrylate (*t*-BA) and ultimately for formation of polyacrylic acid (Si-A$_1$-PAA). The covalent attachment of polyacrylic acid to the silicon surface via an aryl group has been demonstrated by combination of several characterization techniques in one of our previous reports [38]. The graphene conducting additive (EG) used in the fabrication of the composite electrodes is synthesized by electrochemical exfoliation of a natural graphite foil in 0.1 M H$_2$SO$_4$ followed by thermal annealing [51].

2.2. Material characterization

The as-prepared samples were characterized by field-emission gun source scanning electron scanning electron microscope (FEG-SEM; JEOL/JEM-1230) and transmission electron microscopy (TEM, JEOL/JEM-2100F operated at 200 kV). X-ray diffraction (XRD) patterns were recorded using Philips X'Pert MRD X-ray diffractometer using Cu K$_\alpha$ radiation. Thermal gravimetric analysis (TGA) was conducted on a TA instrument (TGAQ50, TA, USA) under a flowing He atmosphere from 30 to 800 °C at a heating rate of 5 °C min^{-1}. Electrical conductivity measurements were made by using a 4-point probe equipment using a